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A PECULIAR TYPE OF INTERCRYSTALLINE BRITTLENESS OF COPPER

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A PECULIAR TYPE OF INTERCRYSTALLINE BRITTLENESS OF COPPER

By Henry S. Rawdon and S. C. Langdon

The following note describing the behavior of copper under rather unusual conditions is believed to be of considerable industrial importance as well as of scientific interest. and is offered here for its suggestiveness rather than as a complete study of the question. The examinations described were made in response to an inquiry addressed to the Bureau of Standards requesting information concerning the embrittlement of copper when heated in a molten salt bath (sodium chloride) for the purpose of cleaning it as well as for softening it. It is well known that metals may be rendered very brittle by electrolytic action in aqueous solutions, in all probability by the action of nascent hydrogen, and it was suspected that perhaps the embrittlement of the copper by means of the molten salt was produced in a somewhat similar manner.

It was found that the copper was in contact more or less with iron (or steel) while immersed in the molten salt. This came about through the use of an iron stirring rod occasionally, iron forceps for handling the pieces, and an iron pot for containing the fused salt. In the electrochemical potential series iron and copper stand some distance apart, copper being electronegative to the iron. Assuming that the two metals bear a similar relation to each other when immersed in a bath of molten salt as they do in an aqueous solution, they would be expected to form a "galvanic couple," the copper being the cathode. By this means the copper might be embrittled, as often happens in aqueous solutions by the action of the liberated hydrogen. In this case, however, the embrittlement must be attributed to some other agent than hydrogen.

To demonstrate how copper may be embrittled under these conditions, two small rods, one of copper and the other mild steel, approximately three-eighths inch diameter, were immersed in a bath of sodium chloride which had been heated somewhat above its fusion point (melting point of sodium chloride, 819° C.) and an emf of approximately 6 volts from a storage battery was impressed upon the system. The copper was made the cathod and the action was continued for several minutes. When removed from the bath, cooled, and tested for brittleness by bending the specimen back and forth while clamped firmly at one end in a vise, the copper rod was found to be very brittle, as compared with a rod of the same length of the untreated copper tested in the same manner. In a similar set-up the copper was made the anode of the electrolytic cell and tested for brittleness in the same manner. In this case the copper proved to be as soft and tough as the original and to require practically the same number of bends to cause it to fracture. It showed no evidence of embrittlement.

Sections of the three rods were examined microscopically in the endeavor to show the cause of the pronounced difference in mechanical properties due to the treatment. The specimens were first plated with nickel, after which a thick layer of copper was deposited electrolytically. This was done so that when the rods were cut and polished for microscopic examination the edge would be protected and the structure of the surface metal could be examined readily up to the extreme edge.

The micrographs illustrate the structure of the material in the three conditions. Fig. 1 shows the copper of the rod used. Though not a hard-drawn rod, the final annealing which was given the metal during its manufacture was not sufficient to remove all evidence of distortion of structure due to cold work. The metal pitted rather badly upon etching, due to inclusions of oxide; the surface of the rod appears rather rough at the magnifications used (× 500) as compared with the same material after treatment in the fused salt.

Fig. 2 shows the copper rod after using it as the anode in the fused-salt electrolytic cell, the cathode being iron. The surface has been smoothed and cleaned so that the edge of the cross section is now an almost perfect arc of a circle. The structure is that of annealed copper, all evidence of cold working has been erased. The inclusions of cuprous oxide are still present but are uniformly distributed and the metal shows nothing in its structure suggestive of brittleness.

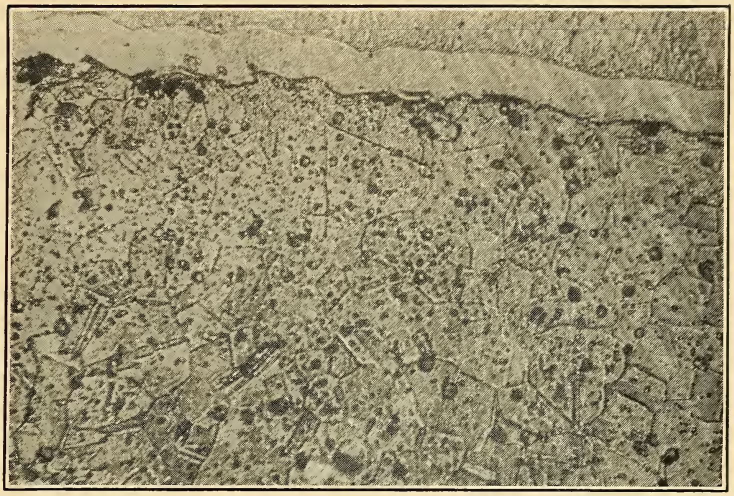


FIG. 1.—*Initial condition of copper rod*

The rod was sectioned transversely. The white band is the layer of nickel, which with the electrolytic copper outside it was used to protect the edge of the section during polishing. The dark spots represent inclusion of cuprous oxide. The etching fluid was concentrated ammonium hydroxide and hydrogen peroxide. ×500

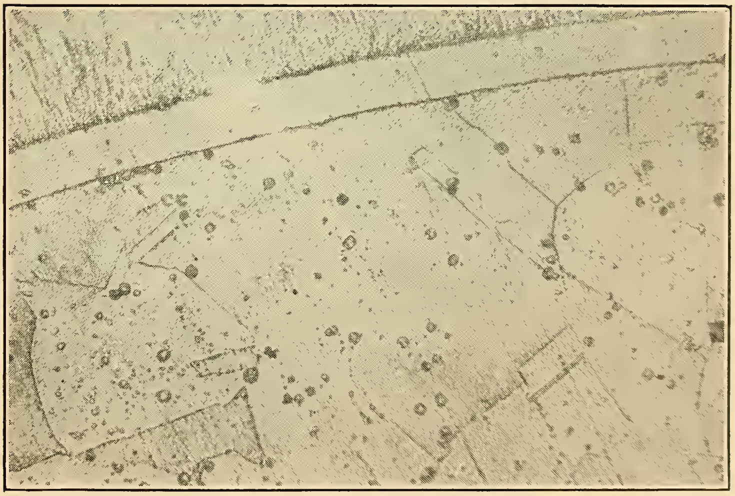
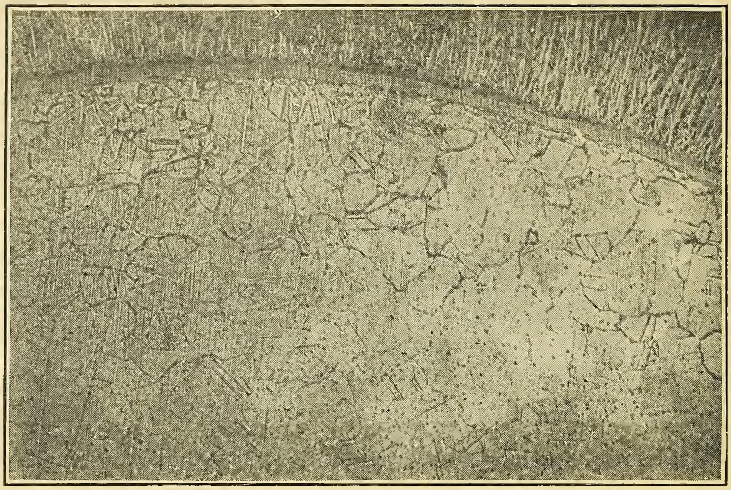
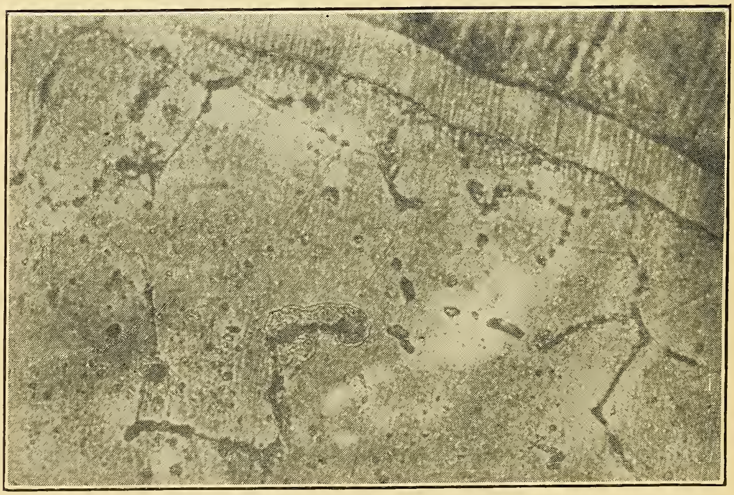


FIG. 2.—*Copper used as anode in fused-salt electrolytic cell*

The high temperature increased the grain size considerably. The edge of the section of the rod has also been smoothed by the etching action of the fused salt. Etching fluid, concentrated ammonium hydroxide and hydrogen peroxide. ×500



(*a*) ×*100*



(*b*) ×*500*

Fig. 3.—*Copper used as cathode in fused-salt electrolytic cell*

The specimen has been slightly etched with the same reagent as in Figs. 1 and 2. A very marked intercrystalline attack of the surface metal occured in the fused-salt bath, by which the grain boundaries are very strongly marked. The surface of the metal was protected as in Figs. 1 and 2

Fig. 3, *a* and *b*, shows the copper rod after its use as the cathode. In Fig. 3, *a* (× 100) a well-defined surface layer is to be seen, in which the crystalline boundaries are very strongly defined. They are to be seen even before the metal is etched. Fig. 3, *b* shows the lightly etched specimen at a higher magnification; the intercrystalline or boundary markings are of an appreciable width and are not merely separations between the grains. The cuprous oxide inclusions are also to be seen distributed much the same as in the other specimens. They do not appear as conspicuous in this specimen as the others, since the metal was etched more lightly.

The probable explanation of embrittlement of the copper when it is made the cathode is that an appreciable amount of metallic sodium is formed by the electrolysis which immediately alloys with the copper. The most striking feature is the selective attack by which the metal of the grain boundaries is acted upon and the action progressed inwardly between the crystals instead of forming an alloy layer upon the outside of uniform thickness. The behavior of the specimen of Fig. 3 when subjected to the bend test is of interest in illustrating the effect of a relatively thin brittle skin upon the properties of a relatively much larger piece. The structure of the interior of the specimen shows no evidence of brittleness any more than does that of the rod used as anode, or the rod in its initial state. It may be assumed, therefore, that only a relatively very thin skin has been rendered brittle by the elctrolytic action; the properties of the entire rod have, however, been very profoundly changed.

WASHINGTON, November 22, 1919.

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